

## PATENT SPECIFICATION

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## (54) IMPROVEMENTS IN ELECTRODES

- (71) We, ROBERT BOSCH GMBH, a German Company, of 4, Breitscheidstrasse, Stuttgart W, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- The present invention relates to improving the activity of platinum and platinum metal alloy catalysts for the anodic oxidation of formic acid and carbon monoxide, particularly in galvanic fuel cells having acid electrolyte.
- It is known to oxidize carbon monoxide and also formic acid in an acid electrolyte using a platinum catalyst. Work with diluted acids below 100°C has been published by NIEDRACH (J. Electrochem. Soc; 109 (1962) 1092.), GILMAN (J. Phys. Chem.; 67 (1963) 1808) and many others. However, the current densities obtained were only a few mA/cm<sup>2</sup>.
- Jasinski et. al (Ber. Bunsenges. Phys. Chemie 68 (1964) 400) used phosphoric acid as electrolyte and obtained a current density of 50 mA/cm<sup>2</sup> at 150°C for the conversion of carbon monoxide.
- Binder et. al (J. Electrochem. Soc; 112 (1965) 355; Fuel Cell Systems, Advances in Chemistry Series 47; 269—282); obtained a current density of 200 mA/cm<sup>2</sup> with Raney Platinum as a catalyst in 3N H<sub>2</sub>SO<sub>4</sub> below 100°C for the conversion of carbon monoxide and also formic acid.
- Of course, the initial polarisation of the electrodes is very high, and therefore the attainable cell voltages in a fuel cell is low. According to tests by Brieter (Electrochem. Acta 10 (1965) 503), Brummer et. al. (J. Phys. Chem. 68 (1964) 1488), and Vielsch (Ber. Bunsenges. 68 (1964) 688), this is attributable to an intermediate product which inhibits the electrode and which can be electro-chemically oxidized only at reference voltages in excess of 500 mV (compared with a hydrogen electrode in the same electrolyte at the same temperature). According to Brieter (Electrochem. Acta; 10 (1965) 503), the inhibiting of the electrode can be clearly demonstrated by the following experiment:
- A platinum electrode in sulphuric acid electrolyte is maintained at a reference voltage of 300 mV by means of a potentiostat. The current is substantially zero, since no oxidizable substances are present in the electrolyte. After formic acid has been added in a concentration of 2 Mol/l, the current increases to about 300 mA/cm<sup>2</sup> in about 1/2 minute, and then drops to about 7 mA/cm<sup>2</sup> within 40 minutes due to the inhibiting of the electrode.
- The present invention therefore provides an electrode for use in a fuel cell utilizing formic acid or carbon monoxide and hydrogen in an acid electrolyte said electrode comprising a skeletal structure, which is inherently electrically conductive or which is electronically conductive by virtue of an electronically conductive additive and a mixed catalyst consisting of a mixture of phosphorus or an element of the VIth main group of the periodic table of elements with platinum metal or a platinum metal alloy, the amount of the former preferably constituting 5 to 95% by volume of the total catalyst volume. The catalyst preferably consists of a mixture of phosphorus, sulphur, selenium, or tellurium with platinum metal, preferably in the form of platinum black, or a platinum metal alloy, preferably an alloy with palladium, iridium, rhodium, ruthenium, molybdenum or silver.
- The electrically conductive skeleton may be manufactured from a powder of a ductile metal, preferably gold or titanium, or from a pulverulent mixture of a plastics material, such as polyacrylonitrile, polyethylene or an epoxy resin, and an electrically conductive material such as graphite or tantalum.
- A phosphorus compound or a compound from group VI of the Periodic

Table may be chemically or electrochemically decomposed in a porous platinum or platinum alloy electrode such that the said element is absorbed by the said metal or metal alloy.

The following is an example of the production of an electrode of the present invention.

#### Example 1

The conventional platinum black catalyst is intimately mixed with selenium powder in the volume ratio 80:20. This mixture, together with gold powder as a skeleton base material and sodium sulphate as a pore forming material, is subsequently pressed in a mould to form a tablet under a pressure of 15 Mp/cm. About 1 g is required for an electrode of 13 mm diameter. The electrode is ready for operation after the sodium sulphate has been dissolved out. It is air-resistant and can be fitted in this form into a fuel cell which is operated by carbon monoxide or formic acid.

The electro-chemical activity is determined in a half cell arrangement by measuring the potential of the electrode under galvanostatic load. The electrode is first of all loaded with 100 mA/cm<sup>2</sup> for 24 hours. A few minutes after the current has been switched on, the reference voltage attains a value which does not vary, or varies only negligibly, during the course of hours. The current density is then varied every 2 hours and the reference voltage is measured.

The current-voltage curve obtained during the conversion of formic acid in 3N H<sub>2</sub>SO<sub>4</sub> at 70°C is plotted as curve 1 in a graph in Fig. 1. The current density is plotted in mA/cm<sup>2</sup> on the abscissa, and the reference voltage is plotted in mV on the ordinate. A current-voltage curve (curve 2) with an identical electrode without a selenium additive is plotted under the same conditions for the purpose of comparison.

The curves for the electrode having a selenium additive show a current density of about 500 mA/cm<sup>2</sup> at a temperature of 70°C and a reference voltage of 200 mV, while at that reference voltage a current density of only 10 mA/cm<sup>2</sup> was observed on the electrode without a selenium additive.

The increase in the activity is even greater at 30°C. Here a current density of about 100 mA/cm<sup>2</sup> is measured for an electrode with a selenium additive at a reference voltage of 200 mV, compared with 0.3 mA/cm<sup>2</sup> on an electrode without a selenium additive. Thus, even at room temperature, a fuel cell provided with the anodes of the present invention can be operated with a current density adequate for technical practicability.

The increase in the activity of the electrodes provided in accordance with the invention is particularly surprising, since these additives themselves are unsuitable as catalysts for fuel

cell electrodes. Sulphur and selenium, are generally known to be highly anti-catalytic.

The increase in activity during the anodic oxidation of carbon monoxide in acid electrolyte was discovered to be equally as great as the increase in activity during the conversion of formic acid. The activity was also determined in a half cell arrangement. For this purpose, the electrode is provided with a gas-supply line and carbon monoxide is blown through the electrode at a slight excess pressure.

The current-voltage curve with the above-described platinum electrode having a selenium additive is plotted as curve 1 in Figure 2 during the anodic oxidation of carbon monoxide in 3N H<sub>2</sub>SO<sub>4</sub> at 70°C. The current density is again plotted in mA/cm<sup>2</sup> on the abscissa, and the reference voltage is plotted in mV on the ordinate. A current-voltage curve (curve 2 in Fig. 2) with a platinum electrode without a selenium additive is again plotted for the purpose of comparison under the same conditions. With a reference voltage of 200 mV this electrode supplies a current of only ~1 mA/cm<sup>2</sup>, whereas the electrode with the addition of selenium (curve 1) supplies a current density of about 160 mA/cm<sup>2</sup> with said reference voltage.

The mixed catalysts utilized in the electrodes of the present invention are specific for the electro-chemical oxidation of formic acid or carbon monoxide with hydrogen. In comparison electro-chemical activity for hydrogen and methanol as possible fuels for fuel cells is not changed, or changed only slightly, in comparison with the normal platinum electrodes. The activity for the conversion of hydrocarbons, for example propane, is even clearly reduced. However, hydrogen and carbon monoxide for example can be converted simultaneously on such an electrode and such a mixture is produced during the conversion of hydrocarbons or carbon.

The excellent resistance of the mixed catalysts also has to be mentioned. The activity of such electrodes was unchanged after weeks in operation.

Further electrodes provided in accordance with the invention will be described by means of the following examples:

#### Example 2

Commercially available platinum black is intimately mixed with selenium powder of the granular size <25 μm in the volume ratio 80:20 in a mortar. This mixture is further mixed with gold powder and sodium sulphate of the granular size 20-60 μm, placed into a mould, and pressed under a pressure of 15 Mp/cm<sup>2</sup>. The electrode is ready for operation after the sodium sulphate has been dissolved out.

#### Example 3

Electrodes of low platinum content are

obtained by commonly precipitating the platinum and the additional element from a salt solution. In this Example, the procedure is based on a hydrochloric acid solution containing 8 g/l hexachloride platonic acid and 60 g/l selenious acid. The solution is heated to 50°C and a 10% hydrazine hydrate solution is then added until all the platinum and selenium has been precipitated. The precipitate is filtered off, washed, and dried in a drying chamber at 120°C. The mixed catalyst thus obtained contains about 10% platinum. It is mixed with graphite powder, polyethylene powder and sodium sulphate in the volume ratio 10:30:25:35 and pressed to form an electrode in accordance with Example 2. The graphite powder should not be too fine, since it would otherwise impair the contact between the polyethylene particles.

Additionally, the mixed catalysts of the electrode of the present invention may contain chemically or electrochemically reduced platinum.

Platinum may be produced electrochemically by electrochemically reducing a platinum compound or a plurality of different platinum containing compounds for example in the manner given in the following preparations.

#### Preparation

Platinum oxide, polyethylene and sodium sulphate are mixed in the volume ratio 30:40:30 and this mixture pressed to form a tablet as described in Example 2. The platonic oxide is reduced cathodically in a potentiostatic half cell arrangement. The electrode is immersed in 3N H<sub>2</sub>SO<sub>4</sub> and connected to a potentiostat which is set +50 mV relatively to a hydrogen reference electrode. The reduction is completed after one hour. The sodium sulphate serving as a pore forming material has simultaneously been dissolved out.

The phosphorus or element of group VI of the Periodic Table is then deposited on the platinum and the electrode is ready for operation.

The phosphorus or an element of group VI of the Periodic Table may be inserted in the electrode by chemically or electrochemically decomposing the phosphorus compound or a compound of an element of group VI of the Periodic Table in a porous platinum or platinum alloy electrode such that the required element is absorbed by the said metal.

#### WHAT WE CLAIM IS:—

1. An electrode for use in a fuel cell utilizing formic acid or carbon monoxide and hydrogen in an acid electrolyte, said electrode

comprising a skeletal structure which is inherently electrically conductive or which is electronically conductive by virtue of an electronically conductive additive and a mixed catalyst consisting of a mixture of phosphorus or an element of the VIth main group of the periodic table of elements with platinum metal or a platinum metal alloy.

2. An electrode as claimed in Claim 1 in which the catalyst consists of a mixture of sulphur, selenium, tellurium or phosphorus with platinum or a metal alloy thereof.

3. An electrode as claimed in Claim 1 or 2 in which the proportion of phosphorus or the group VI element is from 5 to 95 per cent by volume of the total catalyst volume.

4. An electrode as claimed in any of Claims 1 to 3 in which the platinum metal catalyst is platinum black.

5. An electrode as claimed in any of Claims 1 to 3 in which the platinum metal catalyst is Raney platinum.

6. An electrode as claimed in any of claims 1 to 3 in which a platinum metal alloy is present in the mixed catalyst, and the said alloy is an alloy of platinum with palladium, iridium, rhodium, ruthenium, molybdenum or silver.

7. An electrode as claimed in any of Claims 1 to 5 in which the mixed catalyst contains chemically or electrochemically reduced platinum.

8. An electrode as claimed in Claim 6 in which the platinum component and phosphorus or the element of group VI have been co-precipitated from a salt solution.

9. An electrode as claimed in any of Claims 1 to 3 and 7 in which a phosphorus compound or a compound of the element of group VI has been chemically or electrochemically decomposed in a porous platinum or platinum alloy electrode such that the required element is absorbed by the said metal.

10. An electrode as claimed in any of the preceding claims in which the electrically conductive skeleton is manufactured from a powder of a ductile metal.

11. An electrode as claimed in Claim 10 in which said ductile metal is gold or titanium.

12. An electrode as claimed in any of Claims 1 to 9 in which the electrically conductive skeleton is manufactured from a pulverulent mixture of a plastics material and an electronically conductive material.

13. An electrode as claimed in Claim 12 in which said plastics material is polyacrylonitrile, polyethylene or an epoxy resin.

14. An electrode as claimed in Claim 12 or 13 in which said electrically conductive material is graphite or tantalum.

15. An electrode as claimed in Claim 1 substantially as hereinbefore described with reference to any of the foregoing Examples and the accompanying drawings.

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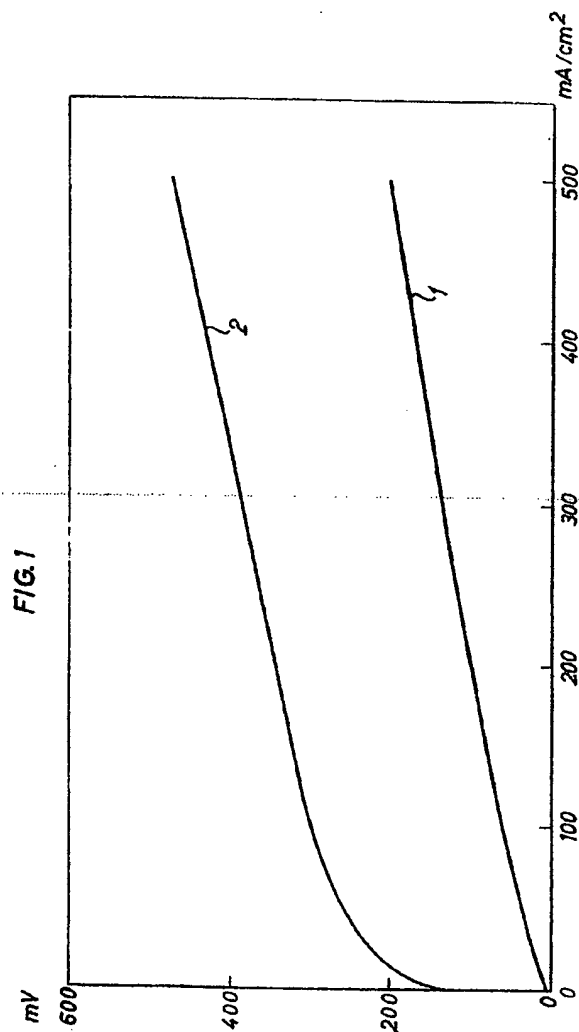
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